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Graphite Re-precipitation in Calcium Graphite Steel*

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Synopsis

Metastable primary cementite precipitates preferentially from the γ solid solution of hypereutectoid Fe-C steels, without stable graphite precipitation, by the ordinary solidifying process. In the present experiment, it was found that graphite re-precipitation readily occurred from the γ solid solution of calcium-treated hypereutectoid cast steels during the air-cooling or the furnace-cooling after the heat-treatment in the γ region from 1060°C to 1210°C. In calcium-untreated cast steels, graphite precipitation was observable mainly along the grain boundaries of dendritic structures by the furnace-cooling from 1000°C immediately after rapid cooling from the molten state to that temperature. If crystal imperfections such as voids are formed in the γ solid solution, the graphite precipitation would more readily occur in those sites, because the activation energy for graphite nucleation decreases due to decreasing interfacial energy and strain energy. On the basis of the experimental results hitherto obtained, the mechanism of graphite precipitation from the γ solid solution was considered.

I. Introduction

In the previous work, it has been made clear that graphite, though usually considered to be difficult to precipitate, precipitates from γ solid solution, instead of primary cementite, when calcium was added to Fe-C steel of hypereutectoid composition in the molten state. Electron-microscopic observation of the graphite precipitated by calcium treatment revealed that non-metallic inclusion consisting of calcium was not present as its nucleus⁽¹⁾. Moreover, the chemical analysis of the graphite extracted by the flame spectrophotometric method⁽²⁾ failed to confirm the existence of calcium in it. However, further examinations should be made of methods suitable to confirm the growth of graphite with the nucleus of calcium-carbide, -sulphide or -oxide when the melt is treated with calcium. Desulphurization and deoxidization of calcium are mainly responsible for the graphite precipitation, besides it is conceivable that the addition of calcium may cause some changes in the physical state of Fe-C alloy in the initial stage of the solidification, which, in turn, will bring about a state favorable to the precipitation of graphite. When crystals crystallize out from a melt, the greater the cooling rate, the more difficult the keeping of a perfect contact with

* The 1409th report of the Research Institute for Iron, Steel and Other Metals. Reported in the J. Japan Inst. Metals, **31** (1967), 1241 (in Japanese).

- (1) T. Ototani, Y. Morooka and Y. Kataura, J. Japan Inst. Metals, **31** (1967), 542.
- (2) H. Gotô and S. Ikeda, *ibid.*, **22** (1958), 185.

the melt will be. So it will be conceivable that a certain number of voids are formed both in the grain boundary and in the grain interior in solidifying process. In general, crystals contain vacancies in thermal equilibrium, and it is well known that their concentration increases exponentially with rising temperature and becomes as large as $10^{-4} \sim 10^{-3}$ near the melting point, and that they get together to form vacancy clusters or voids. It has been reported^{(3)~(6)} that when the diffusion of atoms cannot exceed the rate of solidification, the defects produced at high temperature are quenched, resulting in a supersaturated state.

In the present experiment, to clarify the effect of calcium on the graphite precipitation, hypereutectoid Fe-C alloy containing graphite precipitated from γ solid solution by calcium treatment was re-heated to the range of γ solid solution, water-quenched, air-cooled or furnace-cooled, and whether graphite re-precipitates or primary cementite precipitates, or both graphite and cementite precipitate was examined. Heating for a long time at a high temperature produces many lattice defects like voids, and so this state was examined as to the precipitation of graphite and the mechanism of precipitation of graphite from γ solid solution was considered.

II. Specimens and experimental method

With electrolytic iron, mild steel and swedish pig iron, 2 to 3 kg of hypereutectoid Fe-C alloy was melted in an alumina-lined graphite crucible by a high frequency induction furnace. In Table 1 are shown the chemical compositions of four kinds of cast steel specimen; specimens, SD-1, SD-2 and SD-3 were prepared without calcium treatment, and the other, SD-4 was prepared with calcium treatment. Specimens SD-1, SD-2 and SD-4 were heated at temperatures ranging over from 1060° to 1210°C for 3 to 5 hr in vacuum or in argon atmosphere, and then cooled to room temperature under various cooling conditions. After cutting off the surface of each specimen by 3 to 4 mm their microstructures were examined. 1 kg of specimen SD-3 was cast into an iron mold, and then rapidly

Table 1. Chemical composition of cast steels. (wt %)

Steel	Additional amount of graphitizing agent	Total carbon	Graphite carbon	Si	Mn	P	S	Ca
SD-1	—	1.42	0.033	0.99	0.56	0.011	0.013	—
SD-2	—	1.52	0.025	0.73	0.18	0.018	0.013	—
SD-3	—	1.50	0.022	0.93	0.17	0.018	0.012	—
SD-4	Fe-Ca-Si alloy 1.5%	1.42	0.45	1.02	0.54	0.012	0.012	0.013

(3) R. Maddin and A.H. Cottrell, *Phil. Mag.*, **46** (VII) (1955), 735.

(4) W.W. Mullins, *Acta Met.*, **4** (1956), 421.

(5) A.E. Roswell and A.S. Nowick, *ibid.*, **5** (1957), 228.

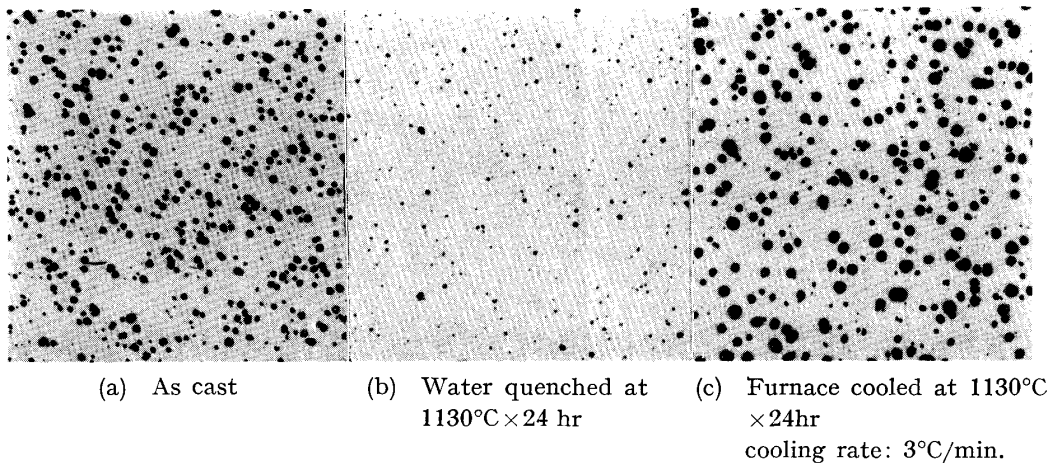
(6) R. Graf, *Compt. rend.*, **246** (1958), 1544.

cooled to 1000°C, from which it was cooled at the same rate as that of CO₂ sand mold in order to quench highly concentrated defects produced in the γ solid solution at around its melting point. The other 1 kg of the same molten steel was cast into a CO₂ sand mold in order to slow somewhat the solidifying rate and then cooled to room temperature, and its microstructure was examined in comparison with those of other specimens.

III. Experimental results

1. Re-precipitation of graphite in hypereutectoid Fe-C alloys treated with calcium

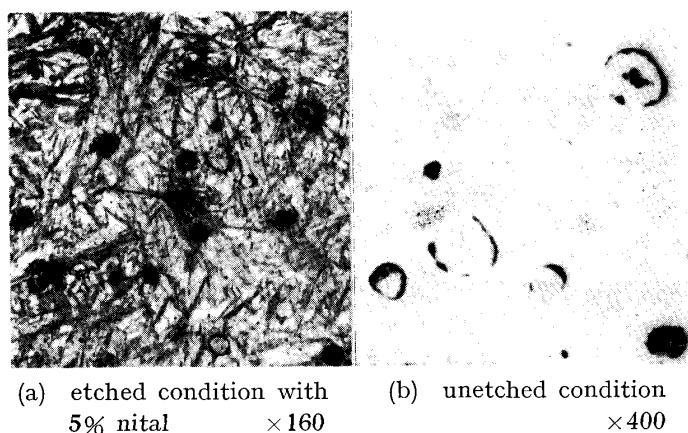
Specimen SD-4 (10 sq. mm \times 10 mml) containing precipitated graphite in as-cast state by the addition of 1.5% of Fe-Ca-Si alloy was heated at 1130°C in argon atmosphere for 5, 24 and 50 hr, subsequently water-quenched, air-cooled and furnace-cooled, and finally precipitated graphite was observed microscopically. Phot. 1 shows typical microstructures. Phot. 1 (a) shows that of the specimen in the cast state before the heat-treatment, in which 0.45% of graphite is precipitated. It was impossible to ascertain that the graphite, existing already in the specimen which was heated at 1130°C for 5 hr and water-quenched, dissolved completely in γ , because graphite was precipitated by about the same amount as in the cast state. However, as clearly seen in Phot. 1 (b), it could be ascertained that the graphite in the specimen heated at 1130°C for 24 hr and water-quenched,



Phot. 1. Graphite re-precipitation of calcium nodular graphite cast steel depending upon heat-treatment in γ region. Specimen SD-4, $\times 25$

dissolved completely in γ , because it was conceivable that graphite could be precipitated in cooling process after water-quenching, the amount of graphite precipitated being very small compared with that in cast state. On the other hand, in the specimens heated under the same condition but cooled in the furnace from 1130° to 500°C at the rate of 3°C per minute, rather a large amount of graphite was re-precipitated, its matrix being pearlite without primary cementite

as shown in Phot. 1(c). It was assumed that the graphite dissolved in γ re-precipitated and grew by diffusion and coagulation in the furnace-cooling process in the range of A_{gr} to A_1 point. Thus, it was seen that graphite, which had precipitated in the γ solid solution, would re-precipitate, instead of precipitation of primary cementite, during cooling even if the graphite would be dissolved by heating in the γ region. In order to confirm further the phenomenon, the specimen was heated at 1130°C for 50 hr and cooled by changing the rate of cooling. As the result, it was seen also that the graphite was re-precipitated in cooling process. It is naturally expected that even in the specimen treated with calcium, graphite once dissolved in the γ solid solution would precipitate primary cementite in cooling process, but that it must be a kind of re-precipitation phenomenon for such a specimen to re-precipitate graphite, from which it will be inferred that the phenomenon is due either to the fact that it is metallurgically stable to precipitate graphite or to the fact that in the γ solid solution a powerful state responsible for an easy precipitation of graphite remains. Consequently, this re-precipitation appears to suggest the mechanism of graphite precipitation in Fe-C alloy of hypereutectoid composition. Phot. 2 shows characteristic microstructures of the specimen heat-treated at 1130°C for 24 hr which correspond to those in Phot. 1 (b). As clearly seen in Photos. 2(a) and (b), the matrix became martensite due to water-quenching and the nodular graphite and the spherulitic graphite shell were present in mixture. Since the spherulitic graphite shell was recognized also in the specimen water-quenched after the heat-treatment at 1130°C for 50 hr, it can be regarded as being formed by diffusion and coagulation of graphite at the boundary surface having many defects in cooling process rather than as a residual fragment of graphite while heating in the γ region. As the lattice defects remained in the boundary between graphite and γ matrix, they are easy to get together even after the graphite had dissolved while heated in the γ region. When hypereutectoid Fe-C alloys in which graphite had precipitated were brought to the homogeneous γ region, it dissolved again in the γ solid solution unless precipitated graphite and



Phot. 2. Spherical graphite shell in water quenched specimen correspond to Phot. 1(b).

graphite resulting from the decomposition of cementite were present in supersaturation; in this case the graphite dissolved interstitially as carbon atoms in the f.c.c. lattice of the γ solid solution. Consequently, many crystal defects remained in the place where graphite was present, after the graphite had dissolved. It can be inferred, therefore, that the voids in the crystal are responsible for the re-precipitation of graphite. These crystal defects, still remaining in the γ solid solution even after the heating at 1130°C, provide favorable sites for the dissolved carbon to diffuse and coagulate while being cooled⁽⁷⁾, which enabled carbon to precipitate as graphite.

2. Graphite precipitation in hypereutectoid Fe-C alloys untreated with calcium

(i) Graphite precipitation from the γ solid solution by heat-treatment at high temperatures

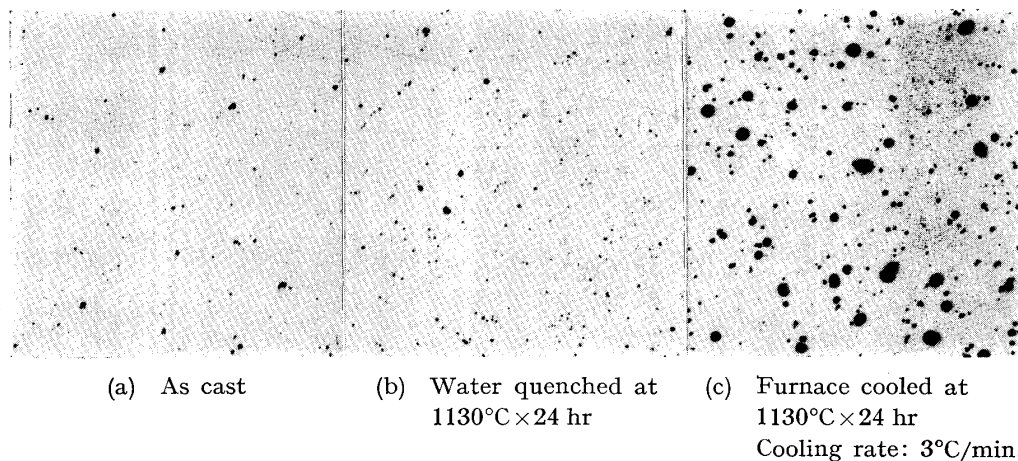
From the results mentioned above it could be expected that graphite would precipitate in the hypereutectoid Fe-C alloys even untreated with calcium provided lattice defects had existed in the γ solid solution. In general, a crystal contains many structural defects such as vacancy, voids, dislocations, etc.; it is well known^{(8),(9)} that the concentration of the vacancy in thermal equilibrium increases exponentially with the rise of temperature. According to Seitz⁽¹⁰⁾, the vacancies combine with one another forming various kinds of defect such as divacancy, trivacancy, cluster and void. Consequently, when ordinary hypereutectoid Fe-C alloys are heated at a high temperature for a long time, they contain many lattice defects. So it was examined whether or not graphite would precipitate in a specimen heat-treated at a high temperature. The specimen SD-1 was heated at 1130°C for 24 hr in argon atmosphere, at which it was water-quenched or furnace-cooled. Phot. 3(a) shows the microstructure in the cast state before the heat-treatment, in which only 0.033% of graphite was present, the matrix being of primary cementite, needle-like cementite and pearlite. Phot. 3(b) shows the microstructure of the precipitated graphite in the specimen heated at 1130°C for 24 hr and water-quenched, and Phot. 3(c) shows that in the specimen heated at 1130°C for 24 hr and furnace-cooled. When the specimen was water-quenched, the graphite precipitation was a little more than that in the specimen of the cast state, but it was very fine and distributed on the grain boundary; that is, the heat-treatment at the γ region may increase the nucleus of graphite precipitation. In the specimen furnace-cooled from 1130°C in 24 hr, the graphite precipitation increased greatly and the matrix was mainly of pearlite, primary cementite being few. In this case, the graphite precipitation was 0.36%, which

(7) M.A. Krishtal, *Phys. Met. and Metallog.*, **7** (1959), 152.

(8) W. Hume-Rothery and G.V. Raynor, *The Structure of Metals and Alloys*, (1954), 303.

(9) W.H. Lomer, *Inst. Metals monograph and report series*, No. 23 (1958), 79.

(10) F. Seitz, *Imperfection in Nearly Perfect Crystals*, (1952), 3.



Phot. 3. Graphite precipitation of calcium-untreated hypereutectoid cast steel depending upon heat-treatment in γ region. Specimen. SD-1, $\times 25$

was about ten times larger than 0.033% of the cast state. In the specimen water-quenched, the graphite precipitation was less, and it is conceivable from the precipitate being very fine that the graphite, resulting from the decomposition of cementite during the heat-treatment at the γ region for a long time, dissolves again. Consequently, it is conceivable that the graphite precipitated in the furnace-cooled specimen results from the diffusion and the coagulation of carbon with some kind of graphite nucleus already present in the γ solid solution in process of cooling from A_{γ} to A_1 point. For example, by heating the specimen at a high temperature in the γ region for a long time, carbon atoms dissolved in voids will diffuse and coagulate rapidly with lower activation energy, becoming easy to form graphite lattice.

Consequently, if the graphite precipitation is closely related with the void, the amount of graphite to precipitate depends upon the temperature and the time of heating in the γ region. Therefore, specimen SD-2 untreated with calcium was heated in vacuum at 1060° and 1210°C for 3 to 7 hr, respectively, and then air-cooled. Fig. 1 shows the number of particles of the graphite by the time for

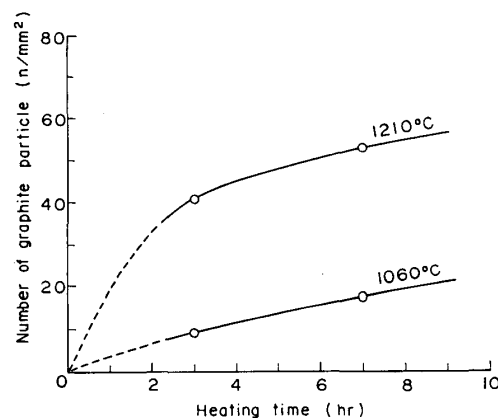
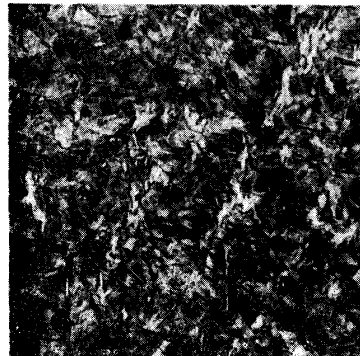


Fig. 1. Number of precipitated graphite particle depending upon heating temperature and heating time. Specimen SD-2.

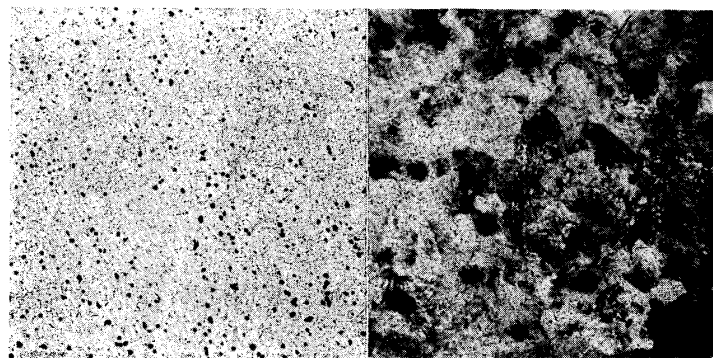
which the specimens were heated, counted under microscope. The number of particles in the precipitated graphite depends upon the heat-treatment in γ region; it tends to become larger with the rise of temperature and to approach saturation with the increase of heating time. It was inferred, therefore, that the presence of crystal defects like the voids, in addition to metallographical factors, might be responsible for the graphite precipitation in the γ solid solution.

(ii) Graphite precipitation from the γ solid solution through the process of rapid solidification

Phot. 4 shows the microstructure in the cast state of specimen SD-3 which was cast into 20 mm ϕ CO₂ sand mold and cooled at the rate of 40°C/min and Phot. 5 shows that of the same specimen SD-3 which was cast into an iron mold and cooled down to 1000°C of the γ region and after holding for 10 minutes at this temperature cooled at the rate of 40°C/min. The amount of graphite precipitated in the case of CO₂ sand mold in which the rate of solidification was comparatively slow, was extremely small, the microstructure of which was composed mainly of primary cementite and pearlite. On the other hand, much graphite precipitated and distributed mainly on the grain boundary in the specimen which was cast in



Phot. 4. The microstructure of as cast state in CO₂ sand mold. Specimen SD-3 etchant, 5% nital. $\times 60$



(a) unetched. $\times 25$ (b) etchant, 5% nital. $\times 160$

Phot. 5. Free graphite precipitated from γ solid solution by the slow cooling from 1000°C after rapid solidification of molten steel up to 1000°C. Specimen SD-3.

the iron mold and cooled rapidly down to 1000°C from which it was cooled down slowly, as shown in Phot. 5(a). In the etched microstructure shown in Phot. 5(b), the primary cementite is hardly observable and the graphite precipitates in the pearlite matrix, the amount being about 0.25%. The reason for this difference in the amount of precipitated graphite is that dissolved carbons diffuse, coagulate and form the graphite lattice at the imperfections produced in process of rapid solidification.

IV. Mechanism of graphite precipitation in γ iron solid solution

In the hypereutectoid Fe-C alloy treated with calcium, graphite precipitated easily from the γ solid solution while it was being cooled. It was found that in this alloy, even without calcium treatment, graphite was capable of precipitation provided the alloy was heat-treated at high temperatures. Hereupon, the mechanism of graphite precipitation in the γ solid solution will be considered, on the basis of the experimental results obtained.

1. Graphite precipitation in homogeneous solid solution

The generation and growth of nucleus will be the pre-requisite for the precipitation of graphite from homogeneous γ solid solution of a hypereutectoid Fe-C alloy. The generation of nucleus begins with a decrease in free energy, some of which are absorbed by interfacial energy of nucleus and by strain energy caused by a volume change due to the nucleation. For a phase change or other processes occurring at constant composition in a solid, the free energy change of forming a particle of the new phase containing i molecules is⁽¹¹⁾:

$$\Delta F_i = \Delta F_{interfacial} + \Delta F_{strain} + \Delta F_v \quad (1)$$

The free energy change in the case of the formation of a spherical nucleus can be expressed as follows⁽¹²⁾:

$$\Delta F_p = 4\pi r^2 \sigma + (4/3)\pi r^3 \varepsilon + (4/3)\pi r^3 \Delta F_v \quad (2)$$

where the first and the second term on the right side are positive, but the third is negative. ΔF_v is the difference in volume free energy between two phases γ and β , σ is the interfacial energy per unit area, and ε represents the elastic strain energy and is assumed to be proportional to the volume of the nucleating sphere. These relations are shown schematically in Fig. 2. In the supersaturated solid solution, with the increase in r , ΔF_p passes through a maximum and then decreases down to negative values. The nucleus smaller than r_0 becomes smaller, and large nucleus grows larger. The critical radius in such a case can be expressed as follows:

$$r_0 = -2\sigma/\Delta F_v + \varepsilon \quad (3)$$

(11) W.M. Mueller, *Energetics in Metallurgical Phenomena*, **1** (1965), 125.

(12) H.K. Hardy and T.J. Heal, *Progress in Metal Physics*, **5** (1954), 143.

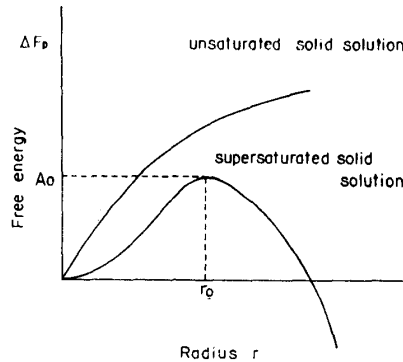


Fig. 2. The free energy of a spherical nuclei as a function of its radius in supersaturated or unsaturated solid solution.

Usually σ is regarded as being independent of temperature, and ΔF_v is temperature-dependent; if ΔH is the heat of transformation or the latent heat, then $\Delta F_v = (\Delta H \cdot \Delta T)/T_E$, where T_E is the equilibrium temperature and ΔT is the amount of supercooling below T_E . Therefore, from Eq. (3),

$$r_0 = \frac{-2\sigma T_E}{\Delta H \cdot \Delta T + \epsilon T_E} \quad (4)$$

When the stable phase β precipitates from the supersaturated phase γ , the values of ΔF_v and ΔH are both negative. It will be seen from Eq. (4) that the critical radius grows smaller when supercooled. The activation energy necessary to form a nucleus of the critical radius larger than r_0 , or the work done to form the surface A_0 can be expressed by the following equations:

$$A_0 = (4/3) \pi r_0^2 \sigma \quad (5)$$

$$A_0 = (16/3) \pi \cdot \sigma^3 / (\Delta F_v + \epsilon)^2 \quad (6)$$

It is seen from these equations that the precipitation will be easy when the activation energy necessary for the nucleation decreases with the increase in the degree of supercooling, whereas the precipitation will be difficult because of the increase in the activation energy caused by the interfacial and the strain energy. Consequently, when a nucleus differs from the original solid solution in crystal structure and is of a larger lattice constant, the activation energy will be fairly great, which makes it difficult to precipitate. Of all the nuclei, the number of those which are larger than that of the critical size can be expressed by $n/N = \exp -A_0/RT$, and the rate of the nucleation by the following equation⁽¹³⁾:

$$I = C_{\text{exp}} - (Q_D + A_0)/RT \quad (7)$$

where Q_D is the activation energy of the diffusion of the solute atom in the solid solution. $(Q_D + A_0)$ is the activation energy of the nucleation at the time of precipitation, and can be calculated when I is measured at each temperature.

(13) R. Becker, *Z. Metallk.*, **29** (1937), 245; *Ann. Physk.*, **32** (1938), 128.

The smaller the value of $(Q_D + A_0)$ is, the easier the precipitation from the hyper-eutectoid solid solution is. The activation energy of the nucleation mentioned above is greatly responsible for the graphite precipitation from the homogeneous γ solid solution.

2. γ iron solid solution containing carbon

What is more important in clarifying the graphite precipitation is the lattice structure of γ iron containing carbon. γ iron is of f.c.c. lattice, the distance between the atoms of iron being 2.58 Å and the lattice constant being $a=3.56$ Å (at 950°C).⁽¹⁴⁾ When carbon is dissolved in γ iron interstitially, the probable sites are considered to be $(1/2, 0, 0)$ and $(1/2, 1/2, 1/2)$.⁽¹⁵⁾ With the amount of carbon in γ iron, the internal energy becomes larger than that of pure γ iron lattice. The excess energy thus increased was brought into existence by the interaction between iron atoms and carbon atoms and between carbon atoms themselves. Takeuchi and Kachi⁽¹⁶⁾ and Kachi and Iwase⁽¹⁷⁾ have reported on these energies, according to which the interaction energy of iron and carbon is 135.98 kcal/mol, making a firm combination. When the concentration of carbon increases, the elastic strain energy of the lattice increases. This strain energy is greater than that of the energy produced by the interaction of carbons, and the carbons tend to get away from one another in γ lattice. As to this, Zener⁽¹⁸⁾ has pointed out from the viewpoint of elasticity that carbons are mutually in repulsive action. What has been said in the above may be confirmed by the activity of carbon in γ lattice. In Fig. 3 are shown the results obtained by Darken and Gurry⁽¹⁹⁾, giving the activity coefficients of carbon at the temperature ranging over from 800° to 1200°C. It is seen that when the concentration of carbon becomes high, it greatly deviates from 1. This shows that it is difficult for carbon to enter inter-

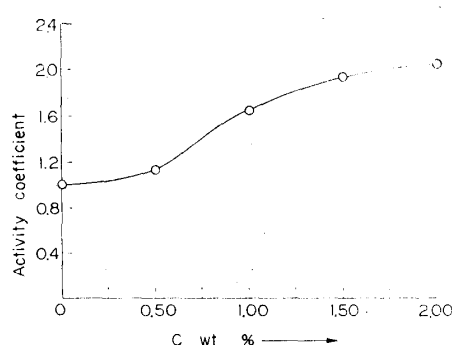


Fig. 3. Activity coefficient of carbon in γ iron (800°~1200°C)⁽¹⁹⁾.

- (14) F. Seitz, *The Modern Theory of Solids*, (1940), 7.
 (15) M. Lipson, *Progress in Metal Physics*, **2** (1950), 1.
 (16) S. Takeuchi and S. Kachi, *J. Japan Inst. Metals*, **B14** (1950), 7.
 (17) S. Kachi and K. Iwase, *ibid.*, **B14** (1950), 1.
 (18) C. Zener, *Phys. Rev.*, **74** (1948), 634.
 (19) L.S. Darken and R.W. Gurry, *Physical Chemistry of Metals*, (1953).

stitially into the lattice as the carbon is highly concentrated, and that with the increase in the concentration of carbon, the γ lattice is elastically strained, resulting in the increase of potential energy.

3. Possibility of graphite precipitation in γ iron solid solution

Even when the hypereutectoid Fe-C alloys are solidified in the usual way, the stable graphite will not precipitate, but only metastable primary cementite precipitates. The reasons for this will be that the probability of forming in the γ solid solution a structure suitable to become Fe_3C is large, and that the distance for carbon atoms to diffuse to form cementite clusters is relatively shorter than that to form graphite. In other words, the activation energy of cementite nucleation is considered to be smaller than that of graphite nucleation. Next, the possibility of graphite precipitation in the ideal γ iron lattice will be considered. Even when carbon atoms in γ iron lattice approach closest to one another, the distance between them is 2.58 Å (at 950°C). Graphite is of a hexagonal layer lattice, and the distance between atoms in the layer is 1.42 Å, that between layers is 3.35 Å, the binding energy of carbon atoms in the layer is 70 to 80 kcal/mol and that between the layers is only 4 kcal/mol.⁽²⁰⁾ Van der Waal's force that combines the layers with one another is rather weak, whereas the force that combines carbon atoms with one another in the layer is of hybrid (SP^2), which hold them in a strong combination⁽²¹⁾. Consequently, carbon atoms in γ lattice coagulate by diffusion to form the clusters of graphite in γ lattice. However, the carbons in γ iron are repulsive to one another and so, the coagulation is difficult. Even if they could coagulate, it is very difficult to form clusters in γ lattice near the graphite lattices, because the distance between those carbons closest to one another is 2.58 Å, which is quite far from the distance 1.42 Å between the graphite lattices. Furthermore, to be precipitated as graphite, it is necessary to form a volume as large as the critical radius r_0 , to which there must be a great resistance. Supposing that a graphite lattice as large as a critical nucleus is to be formed in a perfect γ iron lattice, it is necessary that iron atoms should diffuse to furnish a space to the graphite lattice. This activation energy is about 67.9⁽²²⁾ to 74.2⁽²³⁾ kcal/mol, i.e., the self-diffusion energy of iron. When this energy is combined with the activation energy of carbon diffusion 32 kcal/mol, it becomes $Q_D=100$ to 106 kcal/mol in Eq. (7), and the activation energy of graphite nucleation will be $Q_D+A_0=(100\sim 106+A_0)$ kcal/mol. The activation energy necessary to form a graphite nucleus directly from the hypereutectoid γ iron solid solution has not yet been calculated. However, the energy in the first stage of graphitization of cast iron

(20) M. Yamamoto, Sci. Rep. RITU, A 18-S (1966), 475.

(21) Y.K. Syrkin and M.E. Dyatkina, *Structure of Molecules and the Chemical Bond*, (1950), 298.

(22) F. Seitz and D. Turnbull, Solid State Physics, 6 (1960), 116.

(23) R.F. Mehl and Birchenall, Trans. AIME, 188 (1950), 144.

has been calculated to be 79 kcal/mol.⁽²⁴⁾ This is the activation energy of graphite nucleation when white pig iron is reheated and Fe₃C coexists with it. Strictly speaking, it is not the energy of the graphite nucleation in the homogeneous γ solid solution of the hypereutectoid Fe-C alloy, but it may be considered to be approximately of the same order. A comparison of this value with that mentioned above reveals that $(100 \sim 106 + A_0)$ kcal/mol is too great a value, at which graphite cannot be precipitated by cooling in the sand mold, as the present experiment showed; so the above-mentioned mechanism is unsatisfactory. Consequently, the precipitation of graphite is impossible from a perfect γ iron lattice. As already stated, every metal contains inherently various kinds of structural imperfection, and in the present case, some voids may be favorable for the nucleation of graphite precipitation. The interfacial and the strain energy, which are resistive against the formation of graphite nucleus of the critical size, decrease so much that A_0 in Eq. (6) also decreases, with the result that graphite will precipitate more easily. It is also conceivable that the presence of large numbers of voids will enable graphite to precipitate by air-cooling or by furnace-cooling.

Summary

(1) In calcium-treated hypereutectoid Fe-C alloy which contains precipitated graphite in as-cast state, graphite can easily re-precipitate, but not the primary cementite, by heating the alloy at high temperature of the γ region and successive air-cooling or furnace-cooling.

(2) When the hypereutectoid Fe-C alloy untreated with calcium is heated at the temperature of the γ region or rapidly cooled from the molten state and successively cooled at the rate of 40°C/min from the γ region, graphite will precipitate from the γ solid solution. The number of particles of graphite precipitated depends upon the heat-treatment in the γ region, that is, the number becomes larger when the temperature is high, and tends to approach saturation when the time of heating is longer even when the heat-treatment is done at the same temperature.

(3) The graphite re-precipitation in the homogenous γ solid solution has a close relation with the crystal imperfections such as voids which remain after graphite has dissolved, and solute carbon atoms easily diffuse and coagulate in such places to form graphite lattice.

Acknowledgement

The authors wish to express their gratitude to Prof. S. Koda of the Research Institute for Iron, Steel and Other Metals, Tohoku University for his valuable suggestions.

(24) J. Burke and W.S. Owen, J. Iron Steel Inst., **176** (1954), 147.